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Anomalous Defect Diffusion near the Glass Transition

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by

J. T. Bendler,^a J.J. Fontanella,^a M. F. Shlesinger^b

^aPhysics Department, U.S. Naval Academy, Annapolis, MD 21402-5026, USA

^bPhysical Sciences Division, Office of Naval Research, 800 North Quincy Street,
Arlington, VA 2217-5000, USA

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ANOMALOUS DEFECT DIFFUSION NEAR THE GLASS TRANSITION

John. T. Bendler*, John. J. Fontanella*, Michael. F. Shlesinger[#]

*Physics Department, U.S. Naval Academy, Annapolis, MD 21402-5026

[#]Physical Sciences Division, Office of Naval Research, 800 N. Quincy St., Arlington, VA 22217

ABSTRACT

Anomalous diffusion is employed to model defect motion in materials near their glass transition temperature. Even though the motion of a single defect possesses no characteristic time scale the overall effect of a concentration of defects is to produce stretched exponential relaxation in the glass. This function has a well-defined time scale that depends on the concentration of mobile defects. In our model, the time scale diverges as the temperature is lowered, as well as, increasing with increasing pressure. We use the manner in which this time scale diverges to derive equations for conductivity, dielectric relaxation and viscosity as a function of temperature and pressure that are in good agreement with experimental data.

I. INTRODUCTION

In 1973, Scher and Lax [1], were investigating the ac conductivity of amorphous semiconductors that were used in photocopiers. They employed the fluctuation-dissipation theorem to express the ac diffusion constant $D(\omega)$ in terms of a velocity-

velocity correlation function for mobile charges, i.e.,
$$\text{Re } D(\omega) = \int_{t=0}^{\infty} \cos(\omega t) \langle v(t)v(0) \rangle dt .$$

While a velocity correlation can be more readily applied to situations with particles that

are always in motion, the Scher-Lax problem involved electron hopping between traps with long waiting times between jumps. Focusing on the position of a particle rather than on its velocity they were able to rewrite the ac diffusion constant as,

$$D(\omega) = -\frac{\omega^2}{6} \int_{t=0}^{\infty} e^{-i\omega t} \langle [r(t) - r(0)]^2 \rangle dt .$$

One should next introduce the proper quantum

mechanical Hamiltonian for this problem and calculate $P(r,t) = \left| \langle 0 | \exp(-iHt) | r \rangle \right|^2$ the probability that a particle starting at an origin at time $t=0$ can be found at a site r at time t . Instead, Scher and Lax, following a suggestion by Elliott Montroll, treated the problem classically and used a continuous-time random walk (CTRW) to calculate the position of the particle. The main ingredient of the CTRW was a waiting time probability density function $\psi(t)$ governing how long a particle would be trapped prior to making a jump. For a purely random process $\psi(t)$ would be a simple exponential decay. For the physics of their problem, Scher and Lax derived a $\psi(t)$ that was more complicated and marked by a slow decay that appeared to be algebraic over some time regime.

For a related problem, Scher and Montroll [2] and Shlesinger [3] applied the CTRW formalism to calculate the current generated by these hopping charges when the above system (a thin film of width L) is placed in an electric field. The experimental data was fit by an unusual assumption, that the mean waiting time between jumps was infinite. Mathematically, one chooses for long times that $\psi(t) \propto t^{-1-\beta}$ with $0 < \beta < 1$. Scher called this "dispersive transport" to stress that many time scales entered into the trapping time distribution. It has also been called fractal time transport because the point set of times when jumps occur has a fractal dimension of β [4]. Other terms are subdiffusive, anomalous diffusion, or slow transport. A main result of the calculation for the

average distance a charged particle moves by hopping, in a time t , when placed in an electric field E , that biases the motion in one direction, is given by

$$\langle r(t) \rangle = \sum_r r P(r, t) \propto \bar{r} t^\beta \quad (1)$$

We will assume that \bar{r} , the mean jump distance, is proportional to the electric field, E , i.e. $\bar{r}(E) \propto E$. In a typical experiment, a flash of light creates electron-hole pairs that are pulled apart by the electric field. One set of charges is absorbed near the surface by an opposite polarity electrode and the opposite charged particles transport across the sample. After some time T , the mean position of a packet of charges will be equal to L , the sample width. At that time T ,

$$\langle r(T) \rangle = L \propto \bar{r} T^\beta \quad (2)$$

or by rewriting

$$\frac{1}{T} \propto \left(\frac{E}{L} \right)^{1/\beta} \quad (3)$$

The result for normal transport would be velocity $V = L/T = \mu E$ where μ is a constant, the mobility of the charge. Writing eqn. (3) as $1/T = \mu E/L$ we must find that μ becomes a function of E and L , given by $(E/L)^{\frac{1}{\beta}-1}$.

An effect of the anomalous transport was to break the standard random walk scaling of $r^2 \propto t$ and replace it with $r^2 \propto t^\beta$. This can also be related to writing the diffusion equation with a fractional time derivative of order β .

The introduction of dispersive transport / fractal time transport is elegant and produced a theory able to fit and explain a wealth of data for charge transport in thin films. However, this concept did not readily appear to have general applicability in

condensed matter physics, as it seemed specialized to a particular problem. This changed when fractal time transport was shown to be able to explain the ubiquitous stretched exponential relaxation behavior found in most glassy materials [4].

II. THE CONTINUOUS-TIME RANDOM WALK (CTRW)

The CTRW of Montroll and Weiss [5] is simply a random walk on a lattice with a waiting time distribution $\psi(t)$ governing the time interval between jumps. The lattice is periodic, but the jump times are random. If the random walker reaches a site r at time t , we denote the probability density for this as $Q(r,t)$. We can relate $Q(r,t)$ to the previous jump by

$$Q(r,t) = \sum_s \int_0^t Q(r-s, t-\tau) p(s) \psi(\tau) d\tau + \delta_{r,0} \delta(t) \quad (4)$$

where $p(s)$ is the probability of a jump of displacement s . The delta functions account for the random walk process starting at the origin at time $t=0$. We have written this in one dimension, but using vectors for the displacements allows for this equation to be valid in higher dimensions. Eqn (4) can be solved on a periodic lattice by Fourier transforming over space ($r \rightarrow k$) and Laplace transforming over time ($t \rightarrow u$). Performing these operations, one has

$$\tilde{Q}^*(k,u) = \frac{1}{1 - \tilde{p}(k) \psi^*(u)}$$

where "tilde" represents the Fourier transformed function and "star" represents the Laplace transformed function. The probability that a walker is at site r at time t needs to

take into account the probability $\Phi(\tau)$ that the walker reached r at an earlier time $t - \tau$ and the walker has not left by a time τ later, i.e.

$$P(r, t) = \int_{\tau=0}^t Q(r, t - \tau) \Phi(\tau) d\tau \quad (5)$$

$$\Phi(t) = \int_t^{\infty} \psi(\tau) d\tau \quad \text{so} \quad \Phi^*(u) = \frac{1 - \psi^*(u)}{u}$$

Using the convolution theorem for Laplace transform we can write $P(r, t)$ as

$$\tilde{P}^*(k, u) = \frac{1 - \psi^*(u)}{u} \frac{1}{1 - p(k) \psi^*(u)} \quad (6)$$

In this paper, we will be interested in the number of distinct sites $S(t)$ that a random walker visits within a time t . We will consider the actual jumps to be simple nearest neighbor jumps, but we will allow the waiting time distribution between jumps to have a long tail. Specifically, at long time we will choose

$$\psi(t) \propto t^{-1-\beta}, \quad (t \gg 1) \quad (7a)$$

or equivalently in Laplace space

$$\psi^*(u) \propto 1 - \Gamma(1 - \beta) u^{\beta}, \quad (u \ll 1) \quad (7b)$$

This is the same β that appears in eqns. (1).

To calculate $S(t)$ we need to take into account the number of distinct sites, S_n , visited after n steps and that n steps have occurred by time t ,

$$S(t) = \sum_{n=0}^{\infty} S_n \int_0^t \psi_n(t - \tau) \Phi(\tau) d\tau \quad (8)$$

Setting $z = \psi^*(u)$, the Laplace transform of eqn (8) can be written as

$$\sum_{n=0}^{\infty} S_n z^n \frac{1-\psi^*(u)}{u} \equiv D(z) \frac{1-\psi^*(u)}{u} \quad (9)$$

where, $D(z)$ is the generating function of S_n . We can write S_n in terms of the first passage probability to reach site r for the first time on the n th jump, $F_n(r)$, as

$$S_n = 1 + \sum_r [F_1(r) + \dots + F_n(r)] \quad (10)$$

This allows us to write $D(z)$ as

$$\begin{aligned} D(z) &= \frac{1}{1-z} + z \sum_r F_1(r) + \dots + z^n \sum_r [F_1(r) + \dots + F_n(r)] + \dots \\ &= \frac{1}{1-z} + \frac{1}{1-z} \sum_r [z F_1(r) + \dots + z^n F_n(r) + \dots] \\ &= \frac{1}{1-z} \sum_r F(r, z) \end{aligned} \quad (11)$$

where $F(r, z)$ is the first passage time generating function. Denoting $P_n(r)$ as the probability to visit site r on the n th step, we can relate $F_n(r)$ to $P_n(r)$ via

$$P_n(r) = \sum_{m=0}^n F_{n-m}(r) P_m(0) + \delta_{n,0} \delta_{r,0} \quad (12)$$

This allows one to relate $F(r, z)$ to $P(r, z)$ which is given in Fourier space as

$$\tilde{P}(r, z) = F(r, z) P(r=0, z) + \delta_{r,0} \quad (13)$$

Since,

$$P_{n+1}(r) = \sum_{r'} P_n(r-r') p(r') + \delta_{r,0} \quad (14)$$

then

$$\tilde{P}(k, z) = \frac{1}{1 - z \tilde{p}(k)} \quad (15)$$

Putting this all together one finds that $D(z) = z/[(1-z)^2 P(r=0, z)]$ and the Laplace transform of $S(t)$, in eqn. (8) equals

$$S(z) = \frac{z}{u(1-z) P(r=0, z)}$$

where $z = \psi^*(u)$ (16)

Since, in three dimension $P(r=0, z)$ is not a divergent function of z , the main result using eqns (7a) and (7b) is that

$$S(t) \propto t^\beta \quad (\beta \leq 1) \quad (17)$$

The $\beta = 1$ result holds when the first moment of $\psi(t)$ is finite, and $\beta < 1$ result holds when eqn (7b) is appropriate, i.e. the first moment is infinite.

III. STRETCHED TIMES

A ubiquitous phenomenon in many glassy materials is the appearance of stretched exponential relaxation

$$\phi(t) = \exp\left(-\left(\frac{t}{\tau}\right)^\beta\right), \quad (\beta < 1) \quad (18)$$

This relaxation law has been applied to many materials and many types of relaxation including dielectric, magnetic, volumetric, optical and mechanical. Since a non-integer exponent characterizes the relaxation it might be considered that anomalous diffusion is involved. To obtain anomalous results in the CTRW transport of a particle, we needed waiting times with infinite moments. For the stretched exponential, all of its moments are finite so a connection to fractal time transport seem to be invalidate. Nevertheless, we will show that the effect of the collective motion of a many particles undergoing anomalous transport can lead to the stretched exponential law.

Assume a material has a finite concentration c of mobile defects, that can depend on temperature and pressure. We assume that a site becomes relaxed when it encounters a defect. You may wish to think of a defect as carrying free volume and this allows the material to relax at the defect site. The flux of defects into a site governs its relaxation.

Let $F(r,t)$ be the first passage time probability density function for a defect to *first* reach a site (that we designate as the origin) if the defect starts at $t = 0$ at site, r . We are concerned with relaxation at the origin and in this model it is given by,

$$\begin{aligned}\phi(t) &= \exp[-(\text{flux into origin at time } t)] \\ &= \exp\left(-c \sum_r \int_{\tau=0}^t F(r, \tau) d\tau\right)\end{aligned}\tag{19}$$

where the sum is over all allowable sites for the defects and the integral counts all defects that can reach the origin by time t . Alternatively, if we start a defect at the origin (the site whose relaxation we monitor) and let it hop for a time t , the defect will visit a set of sites $\{r\}$ from which the defect can start and visit the origin within time t . This allows us to rewrite [4] eqn (19) as

$$\phi(t) = \exp(-cS(t))\tag{20}$$

where $S(t)$ is the number of different sites a random walker visits in a time t . For jumps occurring at a regular rate one finds $S(t)$ varying linearly with time providing an exponential relaxation. For our fractal time process with the jumps governed by $\psi(t) \propto t^{-1-\beta}$ one finds that $S(t) \propto t^\beta$ (with $\beta < 1$). This provides a derivation of the stretched exponential law as a probability limit distribution. Since any one of the defects can cause the relaxation, the fractal time motion of many single defects (with an infinite mean waiting time between single jumps) produces the finite moment relaxation law.

In the next section, we consider ions in a glassy polymer. The ions are kicked by the hopping defects and this causes the ions to move. Each defect will have an algebraic waiting time probability, but the ions will have the stretched exponential distribution.

IV. DIVERGENT TIME SCALES

In 1889, Arrhenius [6] introduced the concept of an activation energy Δ together with a law for the related characteristic reaction time $\tau_A = \nu_0^{-1} \exp(\Delta/kT)$ where k is Boltzmann's constant, T is the absolute temperature in degrees Kelvin and ν_0 has the dimensions of frequency. The Arrhenius law was later derived by Kramers in terms of the trajectory of a particle, in a low friction limit, successfully crossing an energy barrier of height, Δ , with an attempt frequency of ν_0 . However the Arrhenius law is typically not valid for most glass-forming materials. A corresponding law for these materials was proposed by Vogel [7] in 1921, for viscosity η in the form $\eta(T) = \eta_\infty \exp((T - T_1)/(T - T_\infty))$. Vogel used this empirical fit for viscosity experiments on mercury, water, and oils. Vogel's law can be written equivalently and more transparently as,

$$\begin{aligned} \eta(T) &= \eta_\infty \exp((T - T_\infty + T_\infty - T_1)/(T - T_\infty)) \\ &= \eta_\infty \exp\left(\frac{T_\infty - T_1}{T - T_\infty} \ln \eta_\infty\right) \end{aligned}$$

Assuming that the viscosity is proportional to a relaxation time scale we can write the above as

$$\tau = A \exp\left(\frac{B}{T - T_0}\right) \quad (21)$$

where T_0 is used instead of T_∞ . This later form was proposed by Fulcher [8] in 1925, and Tammann and Hesse [9] in 1926. Today this is called the Vogel law or the VFT law or some other combination of the above. The interpretation of the parameters A , B and T_0 is not so straightforward. First, one notices that T_0 is a special temperature where the time scale diverges. The temperature T_0 is typically well below T_g , the glass transition temperature of the material, *i.e.*, the relaxation dynamics are focused on T_0 and not on T_g . There have been several attempts to derive the Vogel law or alternative laws. Previously, we had derived the equation for the temperature dependence of the relaxation time at zero pressure [10] in the context of an anomalous defect-diffusion model:

$$\tau_{DD} = A_{DD} \exp\left(\frac{B_{DD}}{(T - T_c)^{3/2}}\right) \quad (22)$$

where A_{DD} , B_{DD} and T_c are constants. We will derive of eqn. () from the time scale of the stretched exponential relaxation law. In the defect diffusion model, the defects unfreeze the parts of the glass that they visit. As the temperature is lowered, defects cluster, and the number of mobile defects decreases. As this occurs, the material becomes more viscous (rigidity begins to set in). At T_g , the defect concentration decreases to the point where rigidity percolates, and the glassy state is formed. Relaxation, however, is still occurring. A phase transition in the number of mobile defects, as the temperature is lowered towards T_c , creates the behavior characterized by eqn. (22).

Equation (22) has consistently been as good as or better than the Vogel law (eqn. 21) for fitting ionic conductivity, dielectric relaxation and viscosity data for glass-

forming materials [11-15]. The Vogel law often fails to fit data adequately near T_g and an Arrhenius law is sometimes used near T_g , in conjunction with a Vogel law in the region above T_g . Equation (22) provides a consistently better fit throughout both regions. In this paper we extended eqn. (22) to include the effect of pressure, but first we need to motivate employing an algebraic waiting time for the defect motion..

There are several ways in which one can arrive at an algebraic waiting time probability density function. If one relates a time scale to overcoming a free energy barrier as follows: $t = t_0 \exp(-(\Delta - TS)/kT)$ then the distributions of energy barriers, Δ , entropies, S , and prefactors, t_0 , can each generate a distribution $\psi(t)$ of waiting times between jumps. Consider first that only S is a random variable and the distribution of environments produces is $f(S) = S_0^{-1} \exp(-S/S_0)$. Then $\psi(t)dt = f(S)dS$ leads at long times to $\psi(t) \approx 1/t^{-1-\beta}$ with $\beta = k/S_0$. When $S < S_0$, $\beta < 1$. For this case, for a single defect, the mean waiting time between jumps, is infinite. If, instead, one places all the randomness in the energy term a similar stretched exponential decay arises, but with the exponent being temperature dependent. In general, both mechanisms can be expected.

Since only the defects are mobile in the model, as the temperature is lowered, the defects cluster (or correlate their motion) to lower the system entropy. We now make the assumption that single defects, of concentration c_1 , are more mobile than a cluster of defects. We therefore replace c in eq. (20) by c_1 . To have a single (isolated) defect at a site, one must first have a defect there with probability c and also have all of the z neighbor sites within its correlation volume unoccupied, i.e.

$$c_1 = c(1 - c)^z \quad (23)$$

with $z = (\xi/d)^3$, where ξ is the defect-defect correlation length, and d is the nearest-neighbor lattice spacing. In a mean field lattice gas model, the correlation length ξ between the defects grows near and above a critical temperature, T_c , as

$$\xi(T) \approx L \left(\frac{T_c}{T - T_c} \right)^{1/2} \text{ where } L \text{ is a constant and } T_c \text{ is the temperature at which single}$$

defects disappear and below which only defect clusters exist. With increasing pressure, the nearest-neighbor spacing d is assumed to decrease isotropically as $d^3 = d_0^3 (1 - \delta(T, P))$ where $1 - \delta(T, P) = V(T, P)/V(T, 0)$ is the fractional volume change of the material as pressure increases and d_0 is the mean lattice spacing separation at zero pressure. The time scale in the stretched exponential can now be expressed as [14-15],

$$\tau \approx c_1^{-1/\beta} \tau_0 = c^{-1/\beta} \tau_0 \exp \left(\frac{BT_c^{3/2}}{(T - T_c)^{3/2} (1 - \delta(T, P))} \right) \quad (24)$$

where $B = -(L/d_0)^3 \ln(1 - c)/\beta$. Note that $=1/\beta$ rescales the prefactor, c , of the exponential. Equation (24) represents a new relaxation law that is Vogel-like, but with a 3/2 temperature exponent and the inclusion of pressure effects. Note that T_c is a function of P . The frequency $1/\tau$ directly provides information about the peak frequency in dielectric relaxation as a function of temperature and pressure.

In an ion-containing polymeric glass-forming material, as described by our model, ion transport is controlled by the defects and it is assumed that the relaxation times for ionic conductivity are the same as those for dielectric relaxation. Consequently, a model

of conductivity can be developed as follows. Although an individual defect has an infinite waiting time between jumps, the ion, hit by a flux of defects, has the stretched exponential waiting time distribution. All the temporal moments of the stretched exponential are finite, including the first moment, which we label as τ_1 . Since, the diffusion constant is of the form $D = \frac{l^2}{6\tau_1}$, employing the Nernst-Einstein relation

$\sigma = \frac{q^2 n D}{kT}$, where q is the charge on an ion and n is the ion concentration

$$\sigma(T, P) = \frac{q^2 n l^2 c^{1/\beta}}{6kT\tau_0} \exp\left(\frac{-BT_c^{3/2}}{(T-T_c)^{3/2}(1-\delta)}\right). \quad (25)$$

Basically, as the pressure is increased, defects are pushed closer together and become more clustered leaving fewer single (mobile) defects. This will decrease the defect flux, increasing the time scale τ , and thus decreasing the conductivity σ .

An equation for the viscosity, η , follows by applying the Stokes-Einstein

equation $\eta = \frac{kT}{6\pi D r_0}$, where r_0 is the effective ion radius.

V. CONCLUSIONS

A defect diffusion model has been developed that is capable of describing the temperature and pressure variation of several dynamical processes in glass-forming materials. The individual defects undergo anomalous diffusion. However, the overall effect of a concentration of defects is normal transport. The basic principle of the model is that electrical relaxation or ionic conduction occurs when a defect encounters a dipole or ion. Each of the parameters in the theory has a clear, physical interpretation. There is

an underlying temperature that represents the temperature below which no defects are mobile. There is a dimensionless constant in the exponent that depends upon the correlation length, separation and concentration of the defects. For dielectric relaxation, the pre-exponential is a product of a characteristic relaxation time (taken to be about that for a lattice vibration) and the defect concentration. The pre-exponentials for ionic conduction and viscosity contain the expected additional terms. Comparison of theory and experiment reveal an excellent representation of the data over a wide range of temperatures and pressures.

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